Viscosity of PbO-SiO₂ Melts

SURESH K. GUPTA

Viscosities (\(\eta\)) of PbO-SiO₂ melts that contained 25.0 to 48.8 mole pct SiO₂ were measured at temperatures 928 to 1273 K by a rotating cylinder method. The data were analyzed in terms of the conventional polymer theory. The results followed Arrhenius behavior in the different temperature ranges despite the general belief of non-Arrhenius behavior of viscosity in slag melts. The calculated activation energies were a function of temperature and composition of the melts. The activation energies for viscous flow, in general, at above approximately 850 °C were lower than those below 850 °C and varied between 25 and 150 kJ per mole.

I. INTRODUCTION

Numerous studies have been made of the viscosity of silicate melts, and comprehensive compilations of data are available for systems of metallurgical interest. Although the temperature dependence of the viscosity of such melts can often be represented by an Arrhenius equation of the form

\[ \eta = \eta_0 \exp \left( \frac{E_a}{RT} \right) \]  

over limited ranges of temperature, it is commonly observed that the apparent activation energy \(E_a\) decreases with increasing temperature over wider ranges.

Such observations have been interpreted variously in terms of hole and free volume theories of liquid state, cooperative motion theory, hybrid theory, environmental relaxation theory, and nonequilibrium statistical mechanics. In a review, Haida and Emi pointed out that hole and free volume theories cannot be regarded as entirely satisfactory except, perhaps, at highly basic compositions where spherical anions such as SiO\(^2\)\(^-\) predominate. At other compositions, as silicate melts contain an array of polyions of varying size, it is difficult to conceive of a specific anion as the flow unit, and some of the parameters in the other theories lose their intended significance.

Danek et al. have shown that at constant temperature, the viscosity of melts in the system CaO-FeO-Fe₂O₃-SiO₂ and CaO-MgO-SiO₂ varied linearly with the average molecular weight of the silicate ions, as calculated by the method of Pretmar. They have suggested that the variation of chain length with temperature may be one of the factors responsible for non-Arrhenius behavior in the viscosity of silicate melts.

In the present study, the viscosities of PbO-SiO₂ melts are reported in the temperature range 928 to 1273 K. Thermodynamic properties of melts of this system have been intensely investigated, and the anionic constitution of these melts is well understood in terms of polymer theory. This work supplements the results reported by Urbain for the same system. The temperature dependence of viscosity was found to exhibit Arrhenius behavior over limited ranges of temperature.

Over wider ranges of temperature, the activation energy for viscous flow was found to decrease with increasing temperature.

II. EXPERIMENTAL

A. Apparatus

Viscosities were measured in air by the rotating cylinder method. Melts were contained in a Pt-20 pct Rh crucible 75 mm long × 25 mm o.d. and 1 mm wall thickness. The crucible was held in a commercial furnace (“Melt Master” Model 6000, Lucifer Furnaces Inc., Washington, PA) equipped with six U-shaped MoSi₂ heating elements. This furnace could be heated to 1000 °C in 2 minutes.

The viscometer and furnace assembly are illustrated in Figure 1. The crucible rested on an alumina platform and was surrounded by a cylindrical alumina muffle (K), 60 mm in diameter. The furnace was closed at the top by a split ceramic block (G) and alumina disc (F) that could be removed to allow visual alignment of the spindle and crucible. The platform that supported the crucible could be raised or lowered by a power-driven elevator assembly (M), which was used for introducing the crucible to the furnace.

The entire furnace rested on a steel platform that could be raised or lowered separately by a manually operated jack. The whole assembly was mounted on wheels and rails. With this arrangement, there was freedom to move the platform horizontally for accurate alignment of crucible and spindle and vertically for positioning the spindle inside the crucible.

For the measurement of viscosity, two commercial Wells-Brookfield digital viscometers (B), (Brookfield Engineering Laboratories Inc., Stoughton, MA, Models RVTD CP and LVTD) each equipped with eight-speed transmissions, were employed, depending on the range required. The signal from the torque measure was fed to a chart recorder. The viscometer was mounted on a stout metal platform (D) (Figure 1) and could be raised or lowered by a rack and pinion device (A) on its own leveling stand. The instrument was calibrated with standard oils, the viscosities of which were certified by the United States National Bureau of Standards.

The crucible-spindle assembly is shown in detail in Figure 2. The spindle of Pt-20 pct Rh consisted of a bob (G) (10 mm diameter × 8 mm long) and shaft (E) (3 mm
Fig. 1—Schematic diagram of the apparatus. A: viscometer stand with rack and pinion device; B: viscometer; C: brass sleeve; D: platform; E: alumina tube; F: alumina disc; G: split ceramic block; H: bob; J: crucible; K: alumina muffle; L: MoSi₂ heating element; M: steel platform; and TC1 and TC2: thermocouples.

Fig. 2—Schematic diagram of spindle and crucible: A: brass sleeve; B: alumina tube; C: platinum wire; D: drilled portion of bob; E: bob shaft; F: slag melt; G: bob; and H: crucible.

diameter × 40 mm long). The shaft terminated at its upper end in an additional portion (D) (10 mm diameter) drilled to receive the lower end of an alumina tube (B) (5.5 mm diameter and 560 mm long) that was attached to the spindle by a loop of stout platinum wire (C), which passed through matching holes in the ceramic and metal parts. The upper end of the alumina tube was cemented to a brass sleeve (A) equipped with a hook by means of which it was suspended from the viscometer, as illustrated in Figure 1.

The temperature was controlled better than ±0.5 °C by thermocouple (TC1) (Figure 1) located close to the heating elements and was measured by thermocouple (TC2) in contact with the base of the crucible. The latter was calibrated against the temperature of the melt in separate experiments by means of a Pt/Pt-13 pct Rh thermocouple immersed directly in the melt, with its tip in the same position as the spindle, i.e., 10 mm from the bottom of the crucible. The variation in temperature with depth for a melt of 12.5 mL vol (30 mm deep) is illustrated in Figure 3. The total variation as measured in this way was 5 °C. This is, presumably, less when the melt is stirred with the spindle.

B. Materials

Silica was prepared by heating analytical reagent grade “silicic acid” (SiO₂·XH₂O) of particle size <100 mesh in a platinum dish at 1050 °C for 6 hours. Maximum impurities (weight percent) were reported as chloride (Cl) 0.01, heavy metals (as Pb) 0.002, Fe 0.001, and nonvolatile with HF 0.2. Litharge (PbO), <60 mesh, was of reported purity 99.9 pct. The intimately mixed powders were melted in a Pt-Rh crucible, and the melts were quenched on a brass plate to yield glasses of the desired compositions. After the viscosities